

Structural Study on a Proton-electron-coupled Organic Conductor: A Hydrogen-bonded Charge Transfer Complex based on Pyridyl-substituted Ethylenedithio-TTF

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1 Introduction

There has been much attention on proton dynamics in hydrogen-bonded (H-bonded) molecular systems in a wide range of scientific fields from chemistry and physics to biology and materials science. For example, in an organic crystalline material, quinhydrone, proton transfer through the intermolecular H-bond associated by electron transfer between the stacked π -electronic systems occurs, to give rise to a unique phase transition. Such a proton-electron-coupled phenomenon is intriguing from both fundamental and applied aspects, however, it has rarely been observed in molecular solids, especially in organic conductors to date.

Recently, we have successfully prepared a new type of proton-electron coupled charge-transfer (CT) complex **1** (Fig. 1a) based on a pyridyl-substituted tetrathiafulvalene (Py-TTF) molecule [1]. Interestingly, the H-bonded proton is located close to the charge-poor (+0.3) donor within the H-bonded unit structure, which causes charge ordering in the TTF stacking column ($\cdots+0.3\cdots+0.7\cdots+0.3\cdots$) in the crystal. This result demonstrates that the π -electrons in the Py-TTF donor column and the H-bonded protons between the donor columns strongly correlate each other. [1].

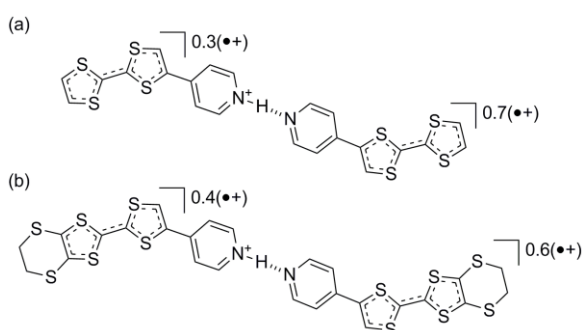


Fig. 1: Chemical structures of the H-bonded unit in (a) Py-TTF complex **1** and (b) Py-EDT-TTF complex **2**.

2 Results and Discussion

In order to gain further insight into this intriguing proton-electron correlated system from the molecular structure viewpoint, in this study, we have newly prepared Py-EDT-TTF complex **2** (Fig. 1b), an ethylenedithio (EDT)-TTF analogue of **1**, and investigated its crystal structure and electronic structure in detail by using

synchrotron radiation at the BL-8A of PF, KEK [2]. As a result, it turns out that the complex **2** also forms a similar unique charge-disproportionated H-bonded unit structure with the $N^+\cdots N$ and N^+-H distance of 2.789(4) Å and 1.18(4) Å. Importantly, by this EDT substitution, the degree of the charge disproportionation is reduced from +0.3 vs. +0.7 in **1** to +0.4 vs. +0.6 in **2**, as revealed by detailed bond length analysis and DFT calculations based on the obtained X-ray diffraction data. Accordingly, the energy barrier and asymmetry of the double-well potential curve of **2** are also lowered, compared to those of **1**. These changes are clearly due to the decrease of the intra-unit Coulomb repulsion derived from expansion of the π -electronic molecular skeleton by the introduction of the EDT group, which proves the presence of a significant coupling between the π -electrons in the TTF skeletons and the H-bonded proton in the unit structure. In addition to this electronic effect, the structural effect of the EDT group, i.e., its steric bulkiness played a crucial role for modulating the overall molecular arrangement (Fig. 2), electronic structure, and conductivity of this proton-electron-coupled organic conductor **2**.

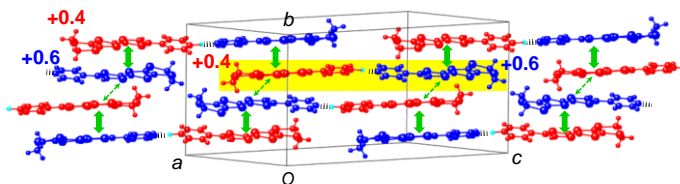


Fig. 2: Molecular arrangement of the charge-disproportionated H-bonded unit (shown in yellow) in **2**. Red and blue colors represent the charge-poor (+0.4) and charge-rich (+0.6) molecules.

References

- [1] S. C. Lee *et al.*, *Chem. Commun.* **48**, 8673 (2012).
 [2] S. C. Lee *et al.*, *Chem. Eur. J.* **20**, 1907 (2014).

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